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Kinetics and Mechanistic Studies of Oxidation of a Ternary Nitrilotri-Acetatocobalt(II) Complexes Involving DL-valine and DL-aspartic Acid as a Secondary Ligands by Periodate

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Abstract: Oxidation of ternary complexes, $[Co^{II}(NTA)(L)(H_2O)_X]^{-n}$ by periodate in aqueous medium has been studied spectrophotometrically over the (25.0 – 45.0) ± 0.1°C range. The reaction show first order kinetics with respect to both $[IO_4^-]$ and the complexes, and the rate of the reaction increases over the $[H^+]$ range (1.05 – 28.20) x 10^{-5} mol dm^{-3} in both cases. Preparation and characterization of $[Co^{II}(NTA)(Asp)(H_2O)_2]^{-3}$ and $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ is performed. Conformation of the formation of the ternary complexes has been done using IR spectrum, TGA, UV-visible spectroscopic and cyclic voltammetry measurements. The thermodynamic activation parameters have been calculated. It is assumed that electron transfer takes place *via* an inner-sphere mechanism.

Keywords: Kinetics, Ternary Co(II) Complexes, Aspartic acid, DL-Valin, UV-spectrophotometer, Inner-Sphere Mechanism, Thermodynamic Activation Parameters

1. Introduction

Amino acid residues are the main constituents of proteins and the study of its sensitivity towards oxidation open up a new area to understand the mechanism involved in the protein and amino acid modification [1].

The use of transition metal complexes of nitrilotriacetic acid have been widely adopted in biology, and are gaining increasing use in biotechnology, particularly in the protein purification technique known as immobilized metal-ion [2].

Ternary complexes of oxygen-donor ligands and heteroaromatic *N*-bases have attracted much interest as they can display exceptionally high stability and biological important [3, 4].

Periodate oxidation exerts a number of biological effects including the enhancement of lymphocyte activation and increased the frequency of effecter to target cell binding [5]. Also, periodate was used in the modification of human serum transferrin by conjugation to oligosaccharide [6].

Oxidation of caffeic acid (3,4-dihydroxycinnamic acid) by means of sodium periodate was reported, that mimics the mechanism of polyphenyleoxidase. The reaction leads to the formation of the antioxidant product 2-S-cysteinylecaffeic adduct which exhibits slightly improved antiradical activity in relation with the parent molecule (caffeic acid) [7]. Also, kinetics studies of periodate oxidations on a series of dextran oligomers, polymers, some dimeric carbohydrates [8] and of chitosans with different chemical composition [9] were investigated to show the dependence of the kinetics on the molecular weight.

Using periodate as an oxidant for inorganic substrates and some transition metals are reported to proceed *via* an inner–sphere mechanism [10-15]. Periodate readily found to oxidize either labile or inert complexes possessing at least one bridging ligand. Initial cobalt(III) products that were transformed to the final cobalt(III) products slowly were identified spectrophotometrically [13-15].

Oxidation of the ternary complexes involving nitrilotriacetatocobaltate(II) succinic acid, $[Co^{II}NS(H_2O)_2]^{3-}$, and nitrilotriacetatocobaltate(II) malonic acid], $[Co^{II}NM(H_2O)_2]^{3-}$ [where N = nitrilotriacetate, S = succinic acid, and M = malonic acid] by periodate has been studied in aqueous medium [16].

Also, oxidation of $[Co^{II}NMa(H_2O)]^{3-}.4H_2O$ and

$[Co^{II}NT(H_2O)]^{3-}.4H_2O$ by periodate have been studied kinetically in aqueous solution [where, N = nitrilotriacetate, Ma = Maleic acid, and T = tartaric acid] over 25 – 45°C and a variety ofpH range [17].

The oxidation of $[Co^{II}(nta)(ox)(H_2O)_2]^{3-}$ and $[Co^{II}(nta)(ph)(H_2O)_2]^{3-}$ (nta = nitrilotriacetate, ox = oxalic acid and ph = phthalic acid) by periodate have been studied kinetically in aqueous solution over 20–40°C and a variety of pH ranges [18], These reactions proceeded via the formation of initial cobalt (III) products, which were converted slowly into final cobalt (III) products fitting an inner-sphere mechanism.

A kinetic study of the oxidation of $[Co(H_2L)(H_2O)_2]^{2+}$ (H_2L = *N*,*N*-bis (salicylaldehyde-1,2-diaminoethane) Schiff base) by periodate in aqueous solution was performed reaction was inhibited as the concentration of Cu(II) increased, and it was independent on Fe(II) concentrations over the ranges studied. An inner-sphere mechanism is proposed for the oxidation pathways of both the protonated and deprotonated Co^{II} complex species [19].

The aim of the present study is to propose the most probable reaction path for the kinetics of oxidation of biologically important ternary nitrilotri-acetatocobalt(II) complexes involving DL-valine and DL-aspartic acid as a secondary ligands. $[Co^{II}(NTA)(L)(H_2O)_X]^{-n}$ where (NTA = nitrilotriactate acid, L= aspartic acid, Val = DL-valin, x= no of coordinated water molecule, and n = no of negative charge).

Choice of these ternary complexes was attributed to two considerations. Firstly, study the effect of aspartate and DL-valin as a secondary ligand on the stability of $[Co^{II}NTA(H_2O)_2]^-$ towards oxidation and the reaction pathways. Secondly, study the effect of secondary ligand on the biological activity of NTA and $[Co^{II}(NTA\ (H_2O)_2]^-$.

2. Experimental

2.1. Materials and Methods

All reagent grade or analar chemicals were used without further purification. $Co(NO_3)_2$ (BDH) solutions were standardized volumetrically with EDTA [20]. A stock solution of $(IO_4)^-$ was made up by weight and covered with aluminum foil to avoid photochemical decomposition [21]. Solutions of NaOAC, HOAC, and $NaNO_3$ were prepared by weighing.

HOAC / NaOAC buffers of known $[H^+]$ were used, and the ionic strength was adjusted with $NaNO_3$.

Potentiometric measurements were performed with a Metrohm 702 SM titrino. The titroprocessor equipped with a 665 dosimat (Switzerland-Heriau). The titroprocessor and electrode were calibrated with standard buffer solution [22].

Calculations were performed using computer program MINIQUAD-75 loaded on an IBM-550 computer. The solution containing 5.0 ml 0.01 mol dm^{-3} complex, 5.0 ml 0.20mol dm^{-3} $NaNO_3$, 5 ml 0.04 mol dm^{-3} HNO_3 and 25 ml deionized water, was titrated with 0.01 mol dm^{-3} NaOH at 25°C.

$Na_3[Co^{II}(NTA)Asp(H_2O)_2]$ and $Na_2[Co^{II}(NTA)\ Val(H_2O)_2]$ were prepared using the same procedure as that for the preparation of $Na_3[Co^{II}NS(H_2O)_2]$ [23]. The elemental analysis data of these complexes are found: C, 25.70; H, 3.02; N, 6.61. Calcd.: C, 24.84; H, 3.11; N, 5.79 and Found: C, 29.46; H, 5.31; N, 6.21; Calcd.:C, 29.66; H, 4.49; N, 6.29, respectively.

IR spectra, thermal gravimetric analysis (TGA), UV Visible spectra and cyclic voltammetric data were carried out to confirm the formula of the complexes.

IR spectra show bands in the (3516 – 3363) cm^{-1} region, were attributed to ν (OH) of the water molecules. The OH of the carboxylic group disappeared and a new (ν COO^-) appeared in the region (1464 – 1432) cm^{-1} indicating that the carboxylic group of the ligands participates in the coordination with the metal ions through deprotonation.

All the spectra of the complexes studied showed asym- (ν COO-Co) band in the region (1582 – 1658) $cm^{-1,}$ the bands in the range (2928 – 2967) cm^{-1} in the spectra, are due to ν (NH) as shown in Figures 1 and 2.

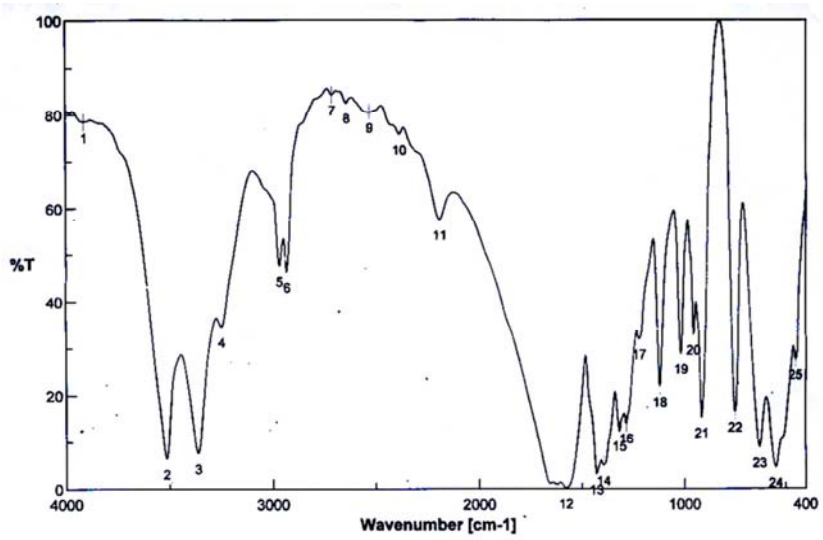

Figure 1. *Infrared spectra of nitrilotriacetatocobalt (II)-Valin[$Co^{II}(NTA)(Val)(H2O)2^{-2}$].*

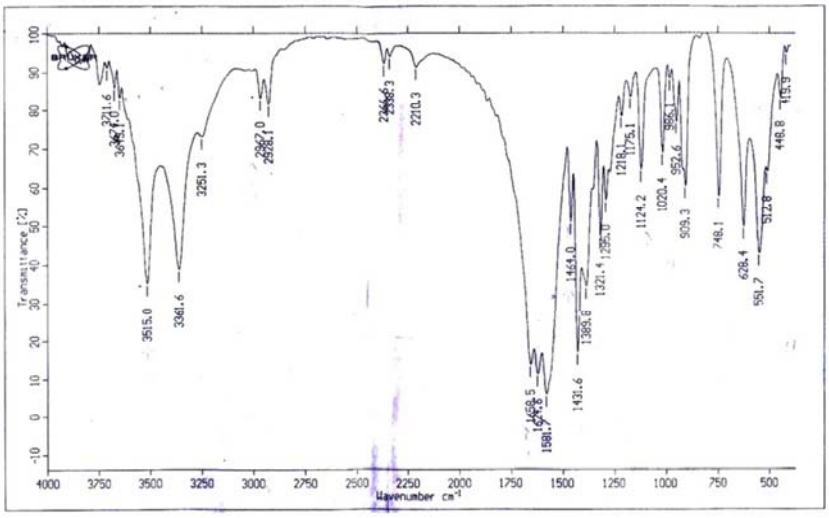

Figure 2. *Infrared spectra of nitrilotriacetatocobalt (II)-Aspartate[Co^{II}(NTA)(Asp)(H2O)2^{-2}].*

The thermogram of the complex $Na_3[Co^{II}(NTA)Asp(H_2O)_2]$ shows weight loss (6.86) at 151.46°C corresponds to the loss of two coordinated water molecule (calc. 7.45), and the weight loss (46.32) at 394.2°C corresponding to the loss five CO_2 molecules (cal. 45.54). While the thermogram of the $Na_2[Co^{II}(NTA)Val(H_2O)_2]$ complex shows weight loss (8.84) at 145.49°C corresponds to the loss of two coordinated water molecules (calc. 8.09), and weight loss (40.62) at 400.64°C corresponding to the loss four CO_2 molecules (cal. 39.55) as shown in Figures 3 and 4.

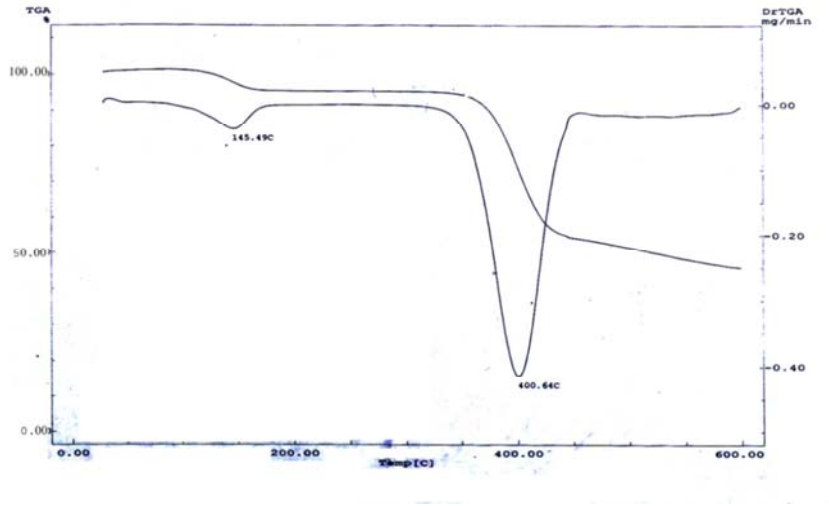

Figure 3. *Thermal decomposition curve of nitrilotriacetatocobalt(II) -Valin[Co^{II}(NTA)(Val)(H2O)2^{-2}].*

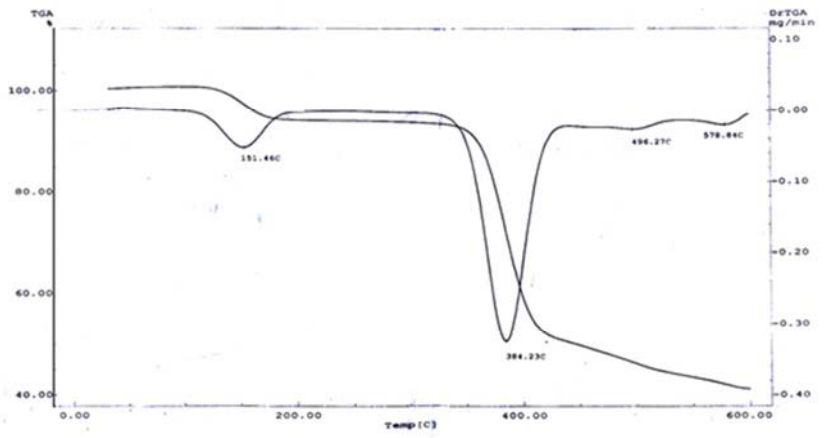

Figure 4. *Thermal decomposition curve of nitrilotriacetatocobalt(II) –Aspartate [Co^{II}(NTA)(Asp)(H2O)2^{-2}].*

Confirmation of the formation of binary and ternary complexes in solution has been carried out by studying the electrochemical behavior (Figures 5-8). Cyclic Voltametric measurements were operated using potentiostat / Galvaostate winking PGS 95 with single-compartment Voltametric cell equipped with a platinum working electrode (area = 0.5 cm^2). A platinum wire was used as counter electrode, and a SCE as reference electrode. A sample volume of 25 cm^2 containing the free metal ion 3 x 10^{-3} mol dm^{-3}, ternary complex 3 x 10^{-3} mol dm^{-3}. All solutions are investigated in water at 30°C, the solutions are purged with nitrogen for 120s, and the potential is scanned at the scan rate 25 MVs^{-1} from (+ 1.5 to –1.0) V.

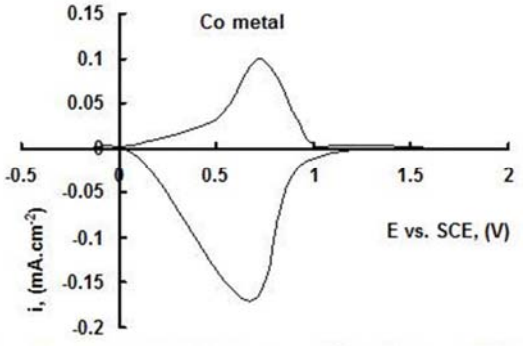

Figure 5. *Cyclic voltammogram for the 3x10^{-3} M of CO(II) solution on Pt electrode at 300K with the scan rate of 25mVs^{-1}.*

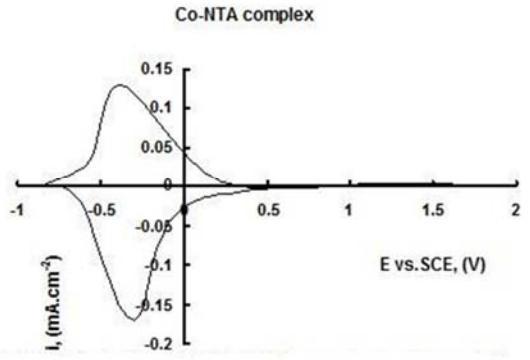

Figure 6. *Cyclic voltammogram for the 3x10^{-3} M of CO(II)-NTA solution on Pt electrode at 300K with the scan rate of 25mVs^{-1}.*

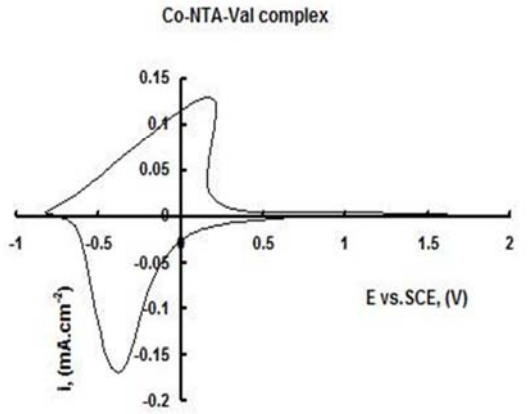

Figure 7. *Cyclic voltammogram for the 3x10^{-3} M of CO(II)-NTA-Val solution on Pt electrode at 300K with the scan rate of 25mVs^{-1}.*

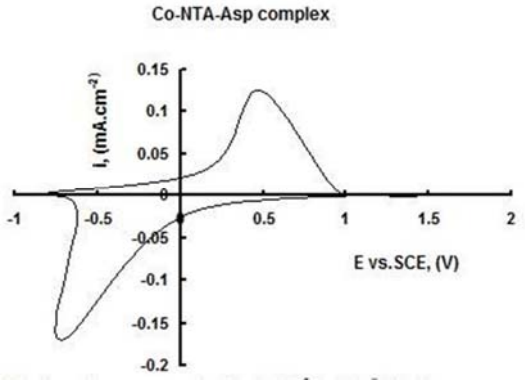

Figure 8. *Cyclic voltammogram for the 3x10^{-3} M of CO(II)-NTA-Asp solution on Pt electrode at 300K with the scan rate of 25mVs^{-1}.*

Metal cobalt ion is difficulty oxidized at more positive potential, +732 mV *vs*. SCE, Figure (3), but the oxidation process of the binary system of Co(II)-nitrilotriacetate becomes slightly easy where the oxidation potential was shifted to more negative value, -375 mV *vs*. SCE, while in the case of ternary complex involving (aspartic with nitrilotriacetato-cobalt(II), the complex become more stable than binary complex, + 478 mV *vs.* SCE), but in case of ternary complex involving (valin with nitrilotriacetato-cobalt(II), the complex become less stable than $Co^{II}(NTA)Asp(H_2O)_2]^{3-}$, because it oxidizes firstly, at +179 mV *vs.* SCE.

2.2. Kinetic Procedures

The U.V.-visible absorption spectra (Figures 9 and 10) of each species of solution containing Co^{II}, $[Co^{II}(NTA)(H_2O)_2]^-$, $[Co^{II}(NTA)(Asp)(H_2O)_2]^{-3}$, $[Co^{II}(NTA)(Val)(H_2O)_2]^{-2}$ at the concentration (4.0×10^{-3} mol dm^{-3}) and $[H^+]$ = 4.36 x 10^{-5} mol dm^{-3} exhibited an absorption bands over the range of 300-700 nm figure (1, 2). The maxima and molar absorptivity of these compounds were collected Table (1). Peaks shifting and molar absorptivity indicated the formation of complex $[Co^{II}(NTA)(Asp)(H_2O)_2]^{-3}$, $[Co^{II}(NTA)(Val)(H_2O)_2]^{-2}$.

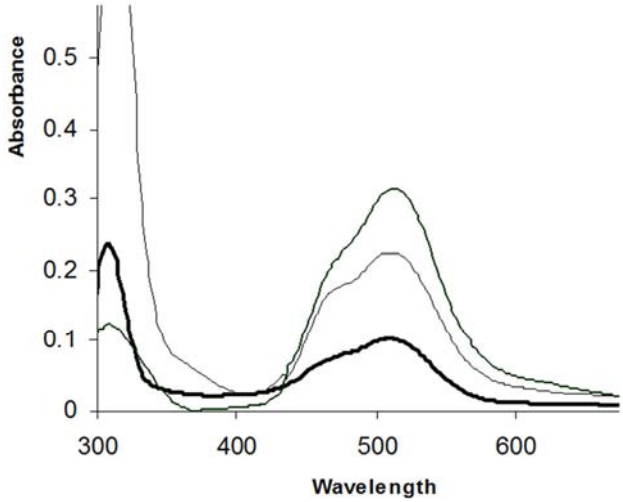

Figure 9. *Change in absorbance for (Co^{II}) ($Co^{II}(NTA)$, and $Co^{II}(NTA)Asp$ at the same concentration (4 x 10^{-3}moldm^{-3}), and pH = 5.*

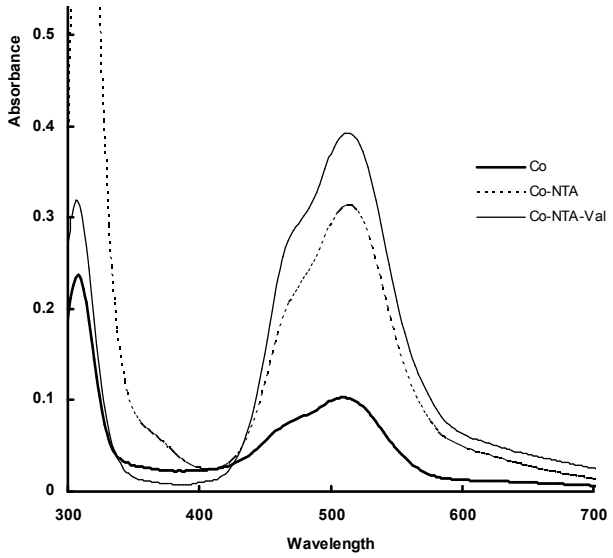

Figure 10. *Change in absorbance for (Co^{II}), Co^{II}(NTA), and Co^{II}(NTA)Val. At the same concentration (4 x 10^{-3}moldm^{-3}), pH = 5.*

Milton-Roy 601 spectrophotometer equipped with a temperature cell holder and connected to a thermo-circulating water bath, was used to measure the oxidation rates by monitoring the absorbance of initial Co^{III} complexes absorbance at 572 and 558 nm, respectively. All reactants, except IO_4^-, were equilibrated at required temperature for 15–20 min. The required amount of separately thermostated IO_4^- stock solution was rapidly mixed, and then the recording of absorbance was commenced.

The $[H^+]$ of the reaction mixture was measured using a Chertsey, Surrey, 7065 pH-meter.

Pseudo-first order conditions were maintained in all runs by the presence of a large excess of IO_4^-, (> 10-fold). The ionic strength was kept constant by addition of $NaNO_3$ solution. The $[H^+]$ of the reaction mixture was found to be always constant during the reaction run.

The error limits for results are calculated using Microcal ™ Origin ® (Version 6.0).

2.3. Oxidation Product

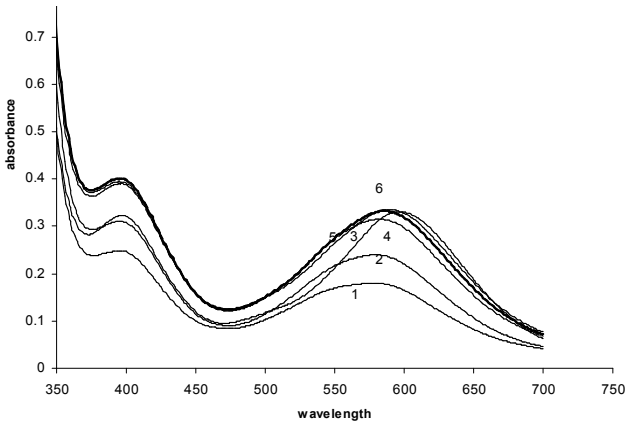

Figure 11. *Change in absorbance as a function of time in the reaction between $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ and $[IO_4]^-$. Curve (6) shows the spectra of the final cobalt (III) product.*

The U.V.-vis. Absorption spectra of the oxidation product of $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ and $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ by periodate were recorded on Jasco UV-530 spectrophotometer as a function of time over the 300-700 nm range (Figures 11 and 12) respectively. The maxima and molar absorptivity coefficients of the final cobalt (III) product at $[H^+]$ = 4.36 x 10-^{5} mol dm^{-3} of oxidation of aspartic ternary complex were ε_{max}^{395} = 158 and ε_{max}^{572} = 135 dm^{3}mol^{-1}cm^{-1}, while the coefficients of the valin ternary complex were ε_{max}^{395} = 156 and ε_{max}^{558} = 157 dm^{3}mol^{-1}cm^{-1}.

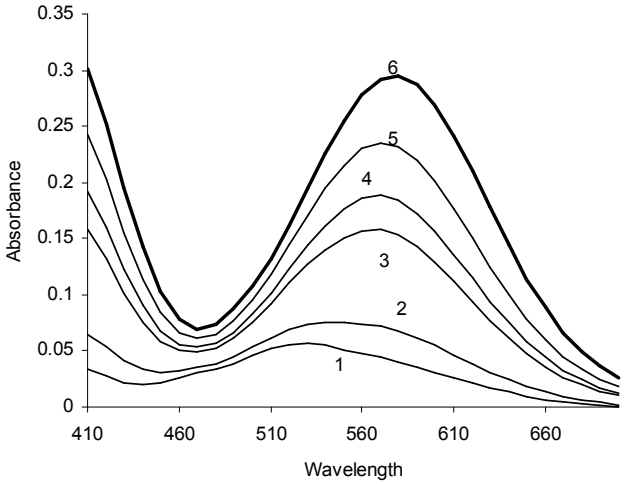

Figure 12. *Change in absorbance as a function of time in the reaction between $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ and $[IO_4]^-$. Curve (6) shows the spectra of the final cobalt (III) product.*

Table 1. *Values of molar absorptiviy $\varepsilon_{max.}$.*

$[Co^{II}]$	ε_{max}^{308} = 59 dm^{3}mol^{-1}cm^{-1}	ε_{max}^{510} = 26 dm^{3}mol^{-1}cm^{-1}.
$[Co^{II}(NTA)(H_2O)]^-$	ε_{max}^{314}= 218 dm^{3}mol^{-1}cm^{-1}	ε_{max}^{512} = 79 dm^{3}mol^{-1}cm^{-1}.
$[Co^{II}(NTA)(Asp)(H_2O)_2]^{-3}$	ε_{max}^{308}= 105 dm^{3}mol^{-1}cm^{-1}	ε_{max}^{512}= 107 dm^{3}mol^{-1}cm^{-1}.
$[Co^{III}(NTA)(Val)(H_2O)_2]^{-2}$	ε_{max}^{306}= 79.67 dm^{3}mol^{-1}cm^{-1}	ε_{max}^{512}= 98.25 dm^{3}mol^{-1}cm^{-1}.

3. Results

Kinetics of $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ and $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$

Oxidation of $[Co^{II}(NTA)L(H_2O)_x]^{n-}$ by $(IO_4)^-$ were studied over a $[H^+]$ range of (1.05 – 28.20) x 10^{-5} mol dm^{-3}, and ionic strength range of 0.30 – 0.60 mol dm^{-3} at 25 – 45ºC using various $(IO_4)^-$ and complex concentrations.

Plots of ln (A_α - A_t) versus time were linear up to 85% of reaction where A_t and A_α are absorbance at time t, and infinity, respectively. Pseudo-first order rate constants, k_{obs}, obtained from the slopes of these plots, Table (2 & 3). These data show that, k_{obs}, was unaffected when the concentration of the Co^{II}- complex was varied at constant $(IO_4)^-$ concentration indicating first order dependence on the complex concentration.

$$d\,[Co^{III}(NTA)L(H_2O)_X]^{n-} / dt = k_{obs}[Co^{II}(NTA)L(H_2O)_x]^{n-}\}_o \quad (1)$$

Plots of k_{obs} against $[IO_4^-]$ were found to be linear, (Figures 13 and 14). The dependence of k_{obs} on $[IO_4^-]$, Table (2 & 3)., is described by

$$k_{obs} = k_1[IO_4^-] \quad (2)$$

The kinetics of the reaction was studied over $[H^+]$ range (1.05 –28.20) x 10^{-5} mol dm^{-3} at different temperatures Table (4 & 5) lists the variation of k_1 with $[H^+]$ at different temperatures which indicate that the reaction rate increased gradually with decreasing $[H^+]$. Plots of k_1 versus $[H^+]$ were linear, with intercepts as shown in (Figures 15 and 16). This behavior can be described by equation 3.

$$k_1 = k_2 + k_3 / [H^+] \quad (3)$$

Values of k_2 and k_3 were calculated at different temperatures, and were listed in Table (6 & 7).

The thermodynamic activation parameters were calculated by using the transition state theory equation. The enthalpies of activation, ΔH^*_2 and ΔH^*_3 for $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ were reported as 44.6 ± 0.12 and 76.9 ± 0.18 kjmol^{-1}, respectively. The corresponding entropies of activation, ΔS^*_2 and ΔS^*_3 were –128.0 ± 0.03 and – 114.4 ± 0.1 $JK^{-1}mol^{-1}$ respectively.

Also, The enthalpies of activation, ΔH^*_2 and ΔH^*_3 for $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ were reported as 49.1 ± 0.12 and 65.8 ± 0.18 kjmol^{-1}, respectively. The corresponding entropies of activation, ΔS^*_2 and ΔS^*_3 were –115.2 ± 0.03 and –153.8 ± 0.1 $JK^{-1}mol^{-1}$ respectively. Furthermore, the reaction rate increased with an increase in ionic strength, over a 0.30 – 0.60 mol dm^{-3} range as shown in Table (2, 3).

From equations 1, 2 and 3 the experimental rate law was derived, as:

$$\text{Rate} = (k_2+k_3/[H^+])\ \{[Co^{II}(NTA)L(H_2O)_x]^{n-}\}_o\ [IO_4^-] \quad (4)$$

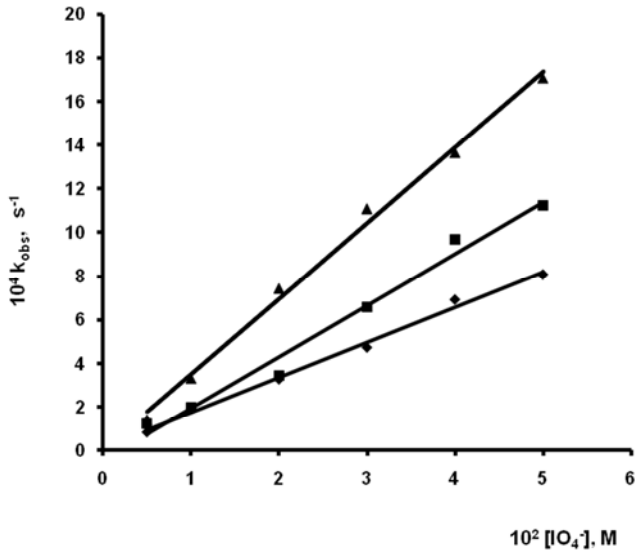

Figure 13. *Variation of k_{obs} versus $[IO_4]^-$ at different temperature for oxidation of $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$.*

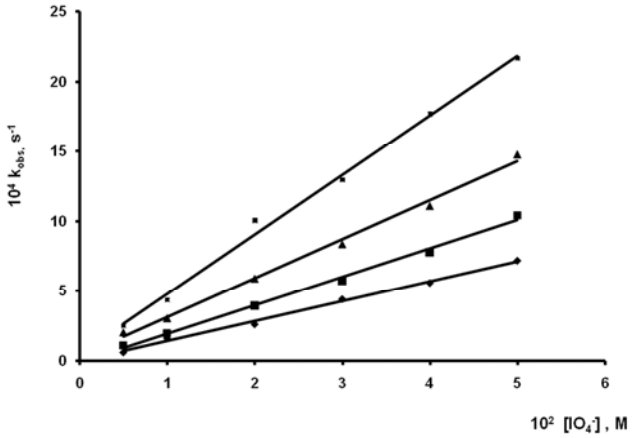

Figure 14. *Variation of k_{obs} versus $[IO_4]^-$ at different temperature for oxidation of $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$.*

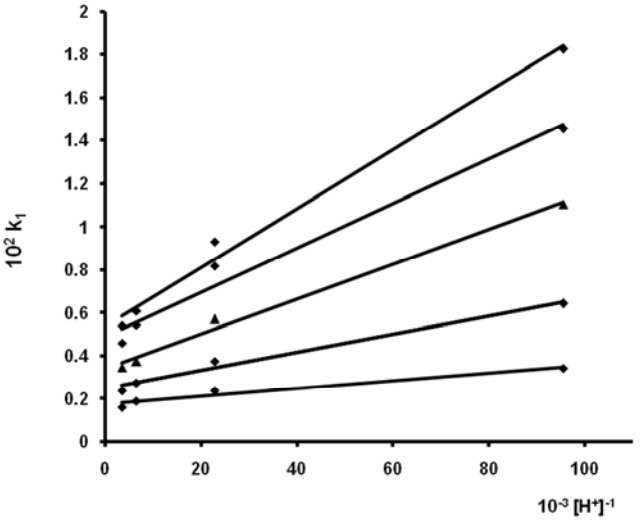

Figure 15. *Variation of k_1 on $[H^+]$ for oxidation of $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$.*

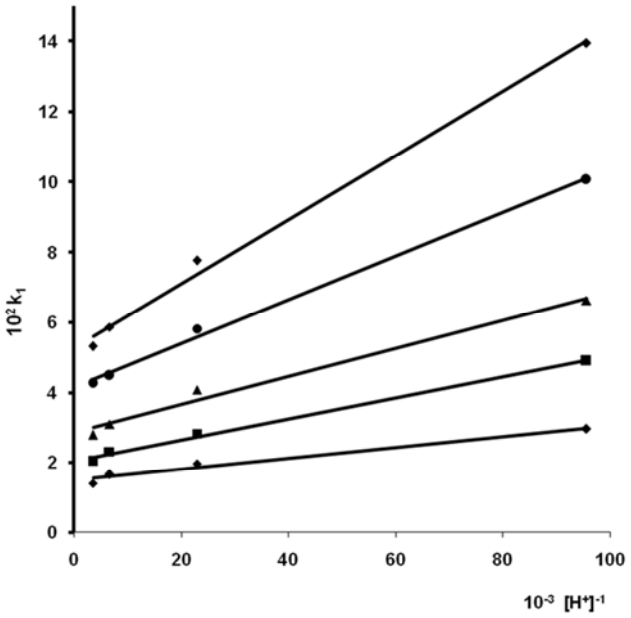

Figure 16. *Variation of k_1 on $[H^+]$ for oxidation of $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$.*

Table 2. *Dependence of the reaction rate constant, $10^4 k_{obs} s^{-1}$, on $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ [a], $[IO_4^-]$, I^b and temperatures at $[H^+] = 28.2 \times 10^{-5}$ mol dm^{-3}.*

$10^2[IO_4^-]$, M	$10^4 k_{obs}$, s^{-1}		
	T = 25º	T = 30º	T = 35º
5.0	8.08 ± 0.04	11.23 ± 0.03	17.05 ± 0.02
4.0	6.93 ± 0.03	9.68 ± 0.04	13.63± 0.01
3.0	4.73 ± 0.01	6.57 ± 0.03	11.07 ± 0.01
2.0	3.27 ± 0.02	3.43 ± 0.02	7.43 ± 0.03
1.0	1.97 ± 0.02	1.93± 0.02	3.30 ± 0.02
0.5	0.83 ± 0.02	1.22 ± 0.12	1.41 ± 0.01

[a]$[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ = 2.0 x 10^{-3} mol dm^{-3}; I^b = 0.25 mol dm^{-3}.
at 10^{3-} $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ = 0.5, 1.0, 3.0 and 4.0 mol dm^{-3}, 35 ºC, I^b,
$[IO_4^-]$= 0.02moldm^{-3}, and $[H^+]$ = 4.36 x 10^{-5} mol dm^{-3}
10^4 k_{obs} = {14.3, 15.1, 12.6 and 14.2 } s^{-1}, respectively. While at (I) = 0.3, 0.4, 0.5, and 0.6 mol dm^{-3}, 35ºC, [a]$[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$, IO_4^-] = 0.02 mol dm^{-3}, an0d $[H^+]$ = 4.36 x 10^{-5} mol dm^{-3} 10^4 k_{obs} = {18.36, 26.20, 29.01 and 36.11} s^{-1}, respectively

Table 3. *Variation of the reaction rate constant, $10^4 k_{obs} s^{-1}$, on [a]$[Co^{II}(NTA)Val(H_2O)_2]^{2-}$, $[IO_4^-]$, I^b [3] at temperatures at $[H^+] = 28.2 \times 10^{-5}$ mol dm$^-$.*

$10^2[IO_4^-]$, M	$10^4 k_{obs}$, s^{-1}		
	T = 25º	T = 30º	T = 45º
5.0	7.18 ± 0.011	8.34 ± 0.011	27.67 ± 0.010
4.0	5.58 ± 0.012	7.20 ± 0.012	20.57± 0.014
3.0	4.40 ± 0.015	5.12 ± 0.011	-------
2.0	2. 62 ± 0.017	3.43 ± 0.015	12.82 ± 0.013
1.0	1.60 ± 0.010	1.97± 0.012	5.78± 0.004
0.5	0.69 ± 0.021	0.95 ± 0.10	3.42± 0.010

[a]$[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ = 2.0 x 10^{-3} mol dm^{-3}; I^b = 0.25 mol dm^{-3}.
at 10^{3-} $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ = 0.5, 1.0, 3.0 and 4.0 mol dm^{-3}, 35 ºC, I^b,
$[IO_4^-]$= 0.02moldm^{-3}, and $[H^+]$ = 4.36 x 10^{-5} mol dm^{-3}
10^4 k_{obs} = {11.4, 12.1, 12.6 and 11.2 } s^{-1}, respectively. While at (I) = 0.3, 0.4, 0.5, and 0.6 mol dm^{-3}, 35ºC, [a]$[Co^{II}(NTA)Val(H_2O)_2]^{2-}$, IO_4^-] = 0.02 mol dm^{-3}, and $[H^+]$ = 4.36 x 10^{-5} mol dm^{-3} 10^4 k_{obs} = {11.16, 13.25, 20.01 and 24.14} s^{-1} respectively

Table 4. *Variation of k_1 with $[H^+]$ at $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ = 2.0 x 10^{-3} mol dm^{-3}, I = 0.25 mol dm^{-3}, different $[IO_4^-]$ and different temperatures.*

105[H+]	102 k1, (M-1s-1)				
mol dm^{-3}	T = 25º	T = 30º	T = 35º	T = 40º	T = 45º
28.2	1.61 ± 0.09	2.37 ± 0.01	3.12 ± 0.09	4.61 ± 0.03	5.38 ± 0.05
15.1	1.90 ± 0.01	2.72 ± 0.02	3.75 ± 0.03	5.45 ± 0.04	6.10 ± 0.06
4.36	2.39 ± 0.01	3.74 ± 0.02	5.71 ± 0.03	8.20 ± 0.05	9.32 ± 0.07
1.05	3.42 ± 0.03	6.43 ± 0.03	11.05 ± 0.04	14.54 ± 0.06	18.26 ± 0.08

Table 5. *Dependence of k_1 with $[H^+]$ at $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ = 2.0 x 10^{-3} mol dm^{-3}, I = 0.25 mol dm^{-3}, different $[IO_4^-]$ and different temperatures.*

$10^5[H^+]$	10^2 k_1, ($M^{-1}s^{-1}$)				
mol dm^{-3}	T = 25º	T = 30º	T = 35º	T = 40º	T = 45º
28.2	1.43 ± 0.06	2.03 ± 0.04	2.79 ± 0.03	4.26 ± 0.02	5.31 ± 0.03
15.1	1.68 ± 0.01	2.31 ± 0.02	3.09 ± 0.02	4.48 ± 0.03	5.87 ± 0.03
4.36	1.97 ± 0.01	2.83 ± 0.02	4.08 ± 0.03	5.82 ± 0.05	7.76 ± 0.04
1.05	2.96 ± 0.03	4.90 ± 0.03	6.62 ± 0.02	10.07 ± 0.06	13.94 ± 0.07

Table 6. *Variation of k_2 and k_3 with temperatures at $[Co^{II}(NTA)Asp(H_2O)_2]^{3-}$= 2.0 x 10^{-3} mol dm^{-3}, I = 0.25 mol dm^{-3}, different $[IO_4^-]$ and different $[H^+]$.*

T, °C	$10^3 k_2$, $M^{-1}s^{-1}$	10^7 k_3, s^{-1}
25	17.52 ± 0.015	1.81 ± 0.010
30	24.63 ± 0.030	4.20 ± 0.009
35	32.40 ± 0.034	8.30 ± 0.010
40	48.84 ± 0.050	10.30 ± 0.013
45	54.04 ± 0.065	13.70 ± 0.017

Table 7. *Variation of k_2 and k_3 with temperatures at $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$= 2.0 x 10^{-3} mol dm^{-3}, I = 0.25 mol dm^{-3}, different $[IO_4^-]$ and different $[H^+]$.*

T, °C	$10^3 k_2$, $M^{-1}s^{-1}$	10^7 k_3, s^{-1}
25	15.01 ± 0.013	1.56 ± 0.014
30	20.53 ± 0.020	3.00 ± 0.019
35	28.59 ± 0.031	4.00 ± 0.012
40	41.49 ± 0.040	6.25 ± 0.023
45	52.78 ± 0.055	9.15 ± 0.019

4. Discussion

The lability of cobalt(II) reactants and the inertness of cobalt(III) products could be utilized as a diagnostic tool for ascertaining inner-sphere electron transfer [10, 13-15]. Oxidation of some cobalt(II) complexes by periodate, where an initial cobalt (III) product was observed, was interpreted in terms of this mechanism.

An inner-sphere mechanism is proposed for the bath way of oxidation of both two Co^{II} complexes $Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ and $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$,. This proposal seems to be supported for the following reasons:

- Formation of the initial cobalt (III) products, which were slowly converted to the final cobalt products [13, 15, 24].
- Periodate ion is capable of acting as a ligand, as evidenced from its coordination to copper(III) [25] and nickel [26].

In aqueous acidic medium the $Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ and $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$, complexes are in equilibria:

$$Co^{II}(NTA)Asp(H_2O)_2]^{3-} \rightleftharpoons [Co^{II}(NTA)Asp(OH)(H_2O)]^{4-} + H^+ K_1 \quad (5)$$

$$Co^{II}(NTA)Val(H_2O)_2]^{2-} \rightleftharpoons [Co^{II}(NTA)Val(OH)(H_2O)]^{3-} + H^+ K_2 \quad (6)$$

K_1 and K_2 were potentiometrically determined as 1.38 x 10^{-6} and 5.01 x10^{-7}, respectively. It was observed from values of K_1 and K_2 at the employed pH range that these equilibriums were not prevailing and the protonated Co^{II}-complex species was the predominant.

In aqueous solutions, periodate species are found in the equilibria [27].

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ (K_3 = 1.0 \text{ X } 10^{-3} \quad (7)$$

$$H_4IO_6^- \rightleftharpoons 2H_2O + IO_4^- (K_4 = 43) \quad (8)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ (K_5 = 5.0 \text{ X } 10^{-6}) \quad (9)$$

Thus, it may be concluded that over the $[H^+]$ range used, the periodate species likely to be present are H_5IO_6 and $H_4IO_6^-$.

The hydrogen ion dependence of the reaction rate of both complexes is in agreement with the involvement of both deprotonated and protonated forms of periodate in the rate determining steps, proceeded by a rapid deprotonation equilibrium and in which both forms are reactive.

The concomitant reaction rate increase with the increase of ionic strength may be attributed to that the reaction rate, in the rate determining step, occurred between two species of the same sign.

In view of the above considerations, kinetics of oxidation of $[Co^{II}(NTA)L(H_2O)_x]^{-n}$ by periodate proceeds by one first – order pathway in each reactant.

The mechanism could be described by the following equations (10-14).

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ K_3 \ (11)$$

$$[Co^{II}(NTA)L(H_2O)_x]^{-n} + H_5IO_6 \rightleftharpoons [Co^{II}(NTA)L(H_5IO_6)(H_2O)_{X-1}]^{-n} + H_2O \ K_6 \ (10)$$

$$[Co^{II}(NTA)L(H_2O)_x]^{-n} + H_4IO_6^- \rightleftharpoons [Co^{II}(NTA)L(H_4IO_6)(H_2O)_{X-1}]^{-(n+1)} + H_2O \ K_7 \quad (11)$$

$$[Co^{II}(NTA)L(H_5IO_6)(H_2O)_{X-1}]^{-n} \rightarrow [Co^{III}(NTA)L(H_5IO_6)(H_2O)_{X-1}]^{(-n+1)} \ k_{10} \quad (12)$$

$$[Co^{II}(NTA)L(H_4IO_6)(H_2O)_{X-1}]^{-(n+1)} \rightarrow [Co^{III}(NTA)L(H_4IO_6)(H_2O)_{X-1}]^{-(n+2)} \ k_{11} \quad (13)$$

From the above mechanism, the rate of the reaction can be described by Equation (14),

$$\text{Rate} = k_{10}K_6 [Co^{II}(NTA)L(H_2O)_x)^{-n}] [H_5IO_6] + k_{11}K_7[Co^{II}(NTA)L(H_2O)_x)^{-n}][H_4IO_6^-] \quad (14)$$

Substituting $[H_4IO_6^-]$ from equation (7) gives,

$$\text{Rate} = [Co^{II}(NTA)L(H_2O)_x)^{-n}] [H_5IO_6] \{k_{10}K_6 + (k_{11}K_7K_3 / [H^+])\} \quad (15)$$

Which is identical to the experimental rate law, Equation (4), and therefore,

$$k_{obs} = \{k_{10}K_6 + (k_{11}K_7K_3 / [H^+])\} [H_5IO_6] \quad (16)$$

Comparison Equations (16) and (2), gives

$$k_1 = k_{10}K_6 + (k_{11}K_7K_3 / [H^+]) \quad (17)$$

Values of k_2 and k_3 were obtained by comparison of Equations (17) and (3), as follows:

$$k_2 = k_{10}K_6 \text{ and } k_3 = (k_{11}K_7K_3)$$

The initial cobalt(III) product of oxidation of $[Co^{II}(NTA)L(H_2O)_x)^{-n}]$ by IO_4^- may be converted to final products according to the equation (18),

$$[NTA(L)Co^{III}\text{-}OIO_3]^{-n} + x\ H_2O \rightarrow [Co^{III}NTA\ (L)(H_2O)_x]^{-n} + I^{VI} \quad (18)$$

Then fast reaction takes place between I^{VI} radicals,

$$2\ I^{VI} \rightarrow IO_4^- + IO_3^- \quad (19)$$

In comparison, using cyclic voltammetric measurements, $Co^{II}(NTA)Asp(H_2O)_2]^{3-}$ is difficulty oxidized at more positive potential, + 478 mV *vs*. SCE. While in the case of $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ the complex is more easy oxidized at less positive potential, + 179 mV *vs*. SCE. Thus the sequence of stability is Asp > Val. Complexes.

According to crystal field theory, Co^{+2} has d^7 distributed as $(t_{2g})^6$ and $(e_g)^1$. Increase of crystal field energy Δ_o between t_{2g} and e_g orbital, by strong field ligands, labilize the free electron in e_g. Values of pK_a for valine and aspartic acid are

2.3 and 1.88 respectively, i.e. strength of conjugate bases are in the sequence Asp > Val. Therefore Δ_o for aspartate ligand is more than both valinate. Thus, loss of e_g electron from the central Co^{+2} ion is easier in case of $[Co^{II}(NTA)Val(H_2O)_2]^{2-}$ than $Co^{II}(NTA)Asp(H_2O)_2]^{3-}$. This is consistent with the order of stability of these complexes.

The high negative entropies of activation for this reaction were climbed to be largely the result of the charge concentration on encounter complex formation, which causes substantial mutual ordering of the solvated water molecules [28]. The intramolecular electron transfer steps are endothermic as indicated by the value of ΔH^*. The contributions of ΔH* and ΔS* to the rate constant seem to compensate each other. This fact suggests that the factors controlling ΔH* must be closely related to those controlling ΔS*. Therefore, the solvation state of the encounter complex would be important in determining ΔH. Thus, the relatively small enthalpy of activation, ΔH*, can be explained in terms of the formation of more solvated complex [29].

Oxidation of Co^{II} complexes shows the formation of an initial Co^{III} product. This may be due to the oxidation process being inner sphere. This is consistent with inner sphere oxidation which is generally proposed for IO_4^- reactions. Through transformation of initial to final Co^{III} product an I^{VI} in the initial product is probably substituted by a water molecule with a slow rate due to inertness of Co^{III} and Co^{II}-OIO_3 bond is being stronger than Co-H_2O bond.

5. Conclusion

Ternary Co^{II} complexes involving NTA and the secondary ligand Valin and Aspartic acid are prepared and their structures were confirmed by different methods.

From the kinetic studies on the oxidation of $[Co^{II}(NTA)(Val)(H_2O)_2^{-2}]$ and $[Co^{II}(NTA)(Asp)(H_2O)]^{-3}$ by periodate, the following results are concluded:-

(1)-The presence of 1/[H+] dependence in the acid medium of the reaction and the rate law suggests involving of the deprotonated form of the cobalt (II) complexes is the reactive species.

(2)-The using of Mn^{++} as a catalyst in the reaction mixture is responsible for the oxidation of the complexes.

(3)-Oxidation of $Co^{II}(NTA)(Val)(H_2O)_2^{-2}]$ and $[Co^{II}(NTA)(Asp)(H_2O)]^{-3}$ is a first –order reaction with respect to $[Co^{II}(NTA)(Asp)(H_2O)]^{-3}$.

(4)-The rate of oxidation of $[Co^{II}(NTA)(Asp)(H_2O)]^{-3}$ is faster than $[Co^{II}(NTA)(Val)(H_2O)_2^{-2}]$ as evidenced from values of electron transfer rate constant for the two complexes.

(5)-The high negative entropies of activation for which reaction were climbed to be largely the result of the charge concentration on the formed encounter complex, which causes substantial mutual ordering of the solvent molecules of the solvated complex. The intramolecular electron transfer steps are endothermic as indicated by the value of ΔH*.

The contributions of ΔH* and ΔS* to the rate constant seem to compensate each other. This fact suggests that the factor controlling ΔH* must be closely related to those controlling ΔS*. Therefore, the solubility state of the encounter complex would be important in determining ΔH*. Thus, the relatively small enthalpy of activation, ΔH*, can be explained in terms of the formation of more solved complex.

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